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<b>(21) International Application Number:</b> PCT/US97/03013 <b>(22) International Filing Date:</b> 27 February 1997 (27.02.97)  <b>(30) Priority Data:</b> 60/012,333 27 February 1996 (27.02.96) US 08/806,693 26 February 1997 (26.02.97) US  <b>(71) Applicant:</b> SOUTHERN CLAY PRODUCTS, INC. [US/US]; 1212 Church Street, Gonzales, TX 78629 (US).  <b>(72) Inventors:</b> DENNIS, Harry, Ryan; P.O. Box 104, Gonzales, TX 78629 (US). LEIGH, John, Scott; 403 Woodlake Drive, McQueeney, TX 78123 (US). RASMUSSEN, Chris, Allen; Route 2, Box 134, Gonzales, TX 78629 (US). BRENNAN, Terrance, P.; Route 4, Box 132, Gonzales, TX 78629 (US).  <b>(74) Agent:</b> RENDA, Barbara, L.; Klauber & Jackson, 411 Hack- ensack Avenue, Hackensack, NJ 07601 (US).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, GH, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> HIGH PERFORMANCE DRY PROCESS ORGANOCLAY COMPOSITIONS, AND METHODS OF USE THEREFOR		
<b>(57) Abstract</b>  An improved organoclay composition which comprises an activated smectite-type clay, a polar aprotic solvent, and a quaternary ammonium compound can be prepared by a dry process and exhibit improved clay dispersion characteristics. These compositions can be used as direct additives to solvent compositions resulting in manufacturing efficiency and cost savings.		

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## HIGH PERFORMANCE DRY PROCESS ORGANOCLAY COMPOSITIONS, AND METHODS OF USE THEREFOR

### BACKGROUND OF THE INVENTION

- 5 This invention relates generally to methods of using activated organoclays, and, more specifically, to the use of activated montmorillonite organoclay compositions which can be used to improve the rheological characteristics of solvent compositions without prior dispersion in an solvent media before addition to the composition.
- 10 Organoclays, representing the reaction product of a smectite-type clay with a quaternary ammonium compound, have long been known for use in gelling of organic liquids such as lubricating oils, linseed oil, toluene and the like. A large variety of highly useful products, such as lubricating greases and paints, are producible through use of such gelling agents. The procedures and chemical
- 15 reactions pursuant to which these organoclays are prepared, are well-known. Thus, under appropriate conditions, the organic compound which contains a cation, will react by ion exchange with the clay which contains a negative layer lattice and exchangeable cations to form the organoclay products.
- 20 Two basic processes are used in the manufacture of organoclays. The first process involves preparing an aqueous dispersion of the clay. This aqueous dispersion is then purified, and the clay is reacted with various organic compounds. The clay is dewatered, dried and milled. This method is commonly referred to as wet process technology. The second method is called dry process technology. It involves the
- 25 mixture of clay and organic compound with, optionally, a small amount of water. This mixture is then subjected to shear, and the resultant organoclay is dried and milled.

Other uses for such modified organoclays are those such as are disclosed in U. S.

30 Patent 5,151,155, wherein organically modified smectite clays are utilized in a process for deinking wastepaper. A problem with the use of dry processed

organoclays in solvent based systems involves the need to predisperse the organoclay in solvent prior to use. A predispersion results in added costs and processing difficulties due to the solvent volumes required in the preparation. As an alternative, expensive wet processing using excessive amounts of quaternary ammonium compounds allows the use of the clay as a direct additive. This approach also has obvious economical implications. A third alternative is to use polar activators to fully disperse the organoclay in the system. This third approach, however, is still known to have severe dispersion limitations when working with dry process organoclays.

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### OBJECTS OF THE INVENTION

It is an object of the present invention to provide dry process organoclay compositions which can be utilized directly as additives to various solvent, and particularly coating, compositions.

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It is further an object of the present invention to prepare solvent compositions, especially coating and paint formulations, by a process whereby the dry process organoclay can be directly added to the solvent composition, without prior dispersion in solvent.

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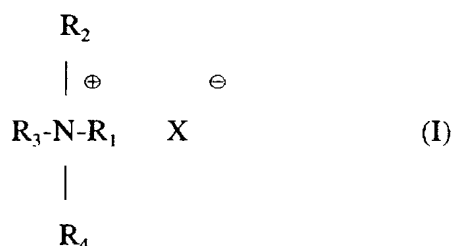
### SUMMARY OF THE INVENTION

In accordance with the present invention, it has unexpectedly been discovered that the activation of smectite-type clays with a mixture of a quaternary ammonium salt and certain aprotic polar compounds during the manufacture of dry process organoclays dramatically improves the resultant organoclay dispersion efficiency when the organoclay is used in coating and paint formulations and other solvent compositions. This improvement enables the use of these dry processed organoclays as direct additives to solvent compositions.

30

Thus, the present invention is concerned with an organoclay composition comprising an activated smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay (active basis), and a polar aprotic compound such as propylene carbonate, ethylene carbonate, N,N-dimethylformamide, N,N-dimethylacetamide and dimethyl sulfoxide and others, and a quaternary ammonium compound of the formula I. The quaternary ammonium compounds which can be utilized in the compositions of the present invention are known agents typically utilized in the preparation of organoclays and include alkyl ammonium compounds of the formula:

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wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from the group consisting of linear or branched, saturated or unsaturated alkyl groups having 1 to 22 carbon atoms, aralkyl groups which are benzyl and substituted benzyl moieties, aryl group, beta, gamma-unsaturated groups having six or less carbon atoms, hydroxyalkyl groups having two to six carbon atoms, and hydrogen, with the proviso that at least one of the substituents is a linear or branched saturated or unsaturated alkyl group; and X is the salt anion.

Preferred ammonium compounds are those such as dimethyl di(hydrogenated tallow) ammonium chloride, benzyl methyl di(hydrogenated tallow) ammonium chloride, dimethyl 2-ethylhexyl hydrogenated tallow ammonium chloride, benzyl dimethyl hydrogenated tallow ammonium chloride and other related ammonium salts.

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### DESCRIPTION OF PREFERRED EMBODIMENTS

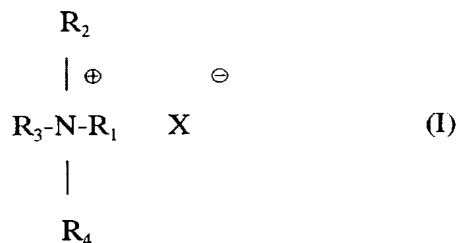
The smectite clays which are utilized as one of the starting materials of the present invention are those which have been conventionally utilized in the prior art.

- 5 Suitable smectite-type clays are those which have a cation exchange capacity of at least 50 milliequivalents (meq.) weight (wt.) per 100 grams of clay (active basis). Useful clays for such purposes include the naturally occurring Wyoming variety of swelling bentonite and similar clays, and hectorite, which is a swelling magnesium-lithium silicate clay. The clays are preferably converted to the sodium form if they  
10 are not already in this form. This can be effected, again as is known in the art, by a cation exchange reaction, or the clay can be converted via an aqueous reaction with a soluble sodium compound.

- Smectite-type clays prepared synthetically can also be utilized, such as  
15 montmorillonite, bentonite, beidelite, hectorite, saponite, and stevensite. Such clays, and processes for their preparation, are described in U. S. Patents 4,695,402, 3,855,147, 3,852,405, 3,844,979, 3,844,978, 3,671,190, 3,666,407, 3,586,478, and 3,252,757, all of which are herein incorporated by reference.

- 20 The polar, aprotic solvents which are suitable for use in the present invention are those such as propylene carbonate, ethylene carbonate, N,N-dimethylformamide, N,N-dimethylacetamide and dimethyl sulfoxide and other related compounds. In the practice of this invention, the use of an organoclay activated with propylene carbonate is particularly preferred.

- 25 The quaternary ammonium compounds which are suitable for use in the present invention are exemplified by the compounds of the formula I. These quaternary ammonium compounds which can be utilized in the compositions of the present invention are known agents typically utilized in the preparation of organoclays and  
30 include alkyl ammonium compounds of the formula:



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wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from the group consisting of linear or branched, saturated or unsaturated alkyl groups having 1 to 22 carbon atoms, aralkyl groups which are benzyl and substituted benzyl moieties, aryl group, beta, gamma-unsaturated groups having six or less carbon atoms, hydroxyalkyl groups having two to six carbon atoms, and hydrogen, with the proviso that at least one of the substituents is a linear or branched saturated or unsaturated alkyl group; and X is the salt anion.

15 In formula I, the aralkyl groups include benzyl and substituted benzyl moieties including fused ring moieties, and have an alkyl portion consisting of linear or branched chains of 1 to 22 carbon atoms. The aryl groups are those such as phenyl and substituted phenyl, including fused ring aromatic substituents.

20 The long chain alkyl groups may be derived from natural occurring oils including various vegetable oils, such as corn oil, coconut oil, soybean oil, cottonseed oil, castor oil and the like, as well as various animal oils or fats such as tallow oil. The alkyl radicals may like wise be petrochemically derived such as from alpha olefins.

25 Representative examples of useful branched, saturated groups include 12-methylstearyl and 12-ethylstearyl. Representative examples of useful branched, unsaturated radicals include 12-methyloley and 12-ethyloley. Representative examples of useful branched, saturated radicals include lauryl, stearyl, tridecyl, myristyl (tetradecyl), pentadecyl, hexadecyl, hydrogenated tallow, docosanyl.

Representative examples of unbranched, unsaturated and unsubstituted groups include oleyl, linoleyl, linolenyl, soya and dehydrogenated tallow.

Examples of aralkyl include benzyl and substituted benzyl moieties such as those  
5 derived from benzyl halides, benzhydryl halides, trityl halides,  $\alpha$ -halo- $\alpha$ -phenylalkanes wherein the alkyl chain has from 1 to 22 carbon atoms, such as 1-halophenylethane, 1-halo-1-phenyl propane and 1-halo-1-phenyloctadecane.

Substituted benzyl moieties, such as would be derived from ortho-, meta- and para-  
10 chlorobenzyl halides, para-methoxybenzyl halides, ortho-, meta and para-nitrilobenzyl halides, and ortho-, meta and para-alkylbenzyl halides wherein the alkyl chain contains from 1 to 22 carbon atoms; and fused ring benzyl-type moieties, such as would be derived from 2-halomethylnaphthalene, 9-halomethylantracene and 9-halomethylphenanthrene, wherein the halo group would  
15 be defined as chloro, bromo, iodo, or any other such group which serves as a leaving group in the nucleophilic attack of the benzyl type moiety such that the nucleophile replaces the leaving group on the benzyl type moiety.

Examples of aryl groups would include phenyl such as in N-alkyl and N, N-dialkyl  
20 anilines, wherein the alkyl groups contain between 1 to 22 carbon atoms; ortho-, meta and para-nitrophenyl, ortho-, meta- and para-alkyl phenyl, wherein the alkyl group contains between 1 and 22 carbon atoms, 2-, 3-, and 4-halophenyl wherein the halo group is defined as chloro, bromo, or iodo, and 2-, 3-, and 4-carboxyphenyl and esters thereof, where the alcohol of the ester is derived from an  
25 alkyl such as carbon atoms, aryl such as phenol, or aralkyl such as benzyl alcohols; fused ring aryl moieties such as naphthalene, anthracene, and phenanthrene.

The  $\beta$ ,  $\gamma$ -unsaturated alkyl group may be selected from a wide range of materials. These compounds may be cyclic or acyclic, unsubstituted or substituted with  
30 aliphatic radicals containing up to 3 carbon atoms such that the total number of



aliphatic carbons in the  $\beta, \gamma$ -unsaturated radical is 6 or less. The  $\beta, \gamma$ -unsaturated alkyl radical may be substituted with an aromatic ring that likewise is conjugated with the unsaturation of the  $\beta, \gamma$ -moiety or the  $\beta, \gamma$ -radical is substituted with both aliphatic radicals and aromatic rings.

5

Representative examples of cyclic  $\beta, \gamma$ -unsaturated alkyl groups include 2-cyclohexenyl and 2-cyclopentenyl. Representative examples of acyclic  $\beta, \gamma$ -unsaturated alkyl groups containing 6 or less carbon atoms include propargyl; allyl(2-propenyl); crotyl(2-butenyl); 2-pentenyl; 2-hexenyl; 3-methyl-2-butenyl; 3-methyl-2-pentenyl; 2,3-dimethyl-2-butenyl; 1,1-dimethyl-2-propenyl; 1,2-dimethylpropenyl; 2,4-pentadienyl; and 2,4-hexadienyl. Representative examples of acyclic-aromatic substituted compounds include cinnamyl (3-phenyl-2-propenyl); 2-phenyl-2-propenyl; and 3-(4-methoxyphenyl)-2-propenyl. Representative examples of aromatic and aliphatic substituted materials include 3-phenyl-2-cyclohexenyl; 3-phenyl-2-cyclopentenyl; 1, 1-dimethyl-3-phenyl-2-propenyl; 1,1,2-trimethyl-3-phenyl-2-propenyl; 2,3-dimethyl-3-phenyl-2-propenyl; 3,3-dimethyl-2-phenyl-2-propenyl; and 3-phenyl-2-butenyl.

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The hydroxyalkyl group is selected from a hydroxyl substituted aliphatic radical wherein the hydroxyl is not substituted at the carbon adjacent to the positively charged atom, and the group has from 2 to 6 aliphatic carbons. Representative examples include 2-hydroxy-ethyl (ethanol); 3-hydroxypropyl; 4-hydroxypentyl; 6-hydroxyhexyl; 2-hydroxypropyl (isopropanol); 2-hydroxybutyl; 2-hydroxypentyl; 2-hydroxyhexyl; 2-hydroxycyclohexyl; 3-hydroxycyclohexyl; 4-hydroxypentyl; 2-hydroxycyclopentyl; 3-hydroxycyclopentyl; 2-methyl-2-hydroxypropyl; 1,1,2-trimethyl-2-hydroxypropyl; 2-phenyl-2-hydroxyethyl; 3-methyl-2-hydroxybutyl; and 5-hydroxy-2-pentenyl.

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A preferred compound of Formula I contains at least one linear or branched, saturated or unsaturated alkyl group having 12 to 22 carbon atoms and at least one

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linear or branched, saturated or unsaturated alkyl group having 1 to 12 atoms. The preferred compound of Formula I may also contain at least one aralkyl group having a linear or branched, saturated or unsaturated alkyl group having 1 to 12 carbons in the alkyl portion. Mixtures of these compounds may also be used.

5

Especially preferred compound of Formula I is a compound where  $R_1$  and  $R_2$  are hydrogenated tallow,  $R_3$  and  $R_4$  are methyl or where  $R_1$  is hydrogenated tallow,  $R_2$  is benzyl and  $R_3$  and  $R_4$  are methyl or a mixture thereof such as 90% (equivalents) of the former and 10% (equivalents) of the latter.

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The salt anion of the ammonium salt may be methosulfate, ethosulfate, methylcarbonate, ethylcarbonate, chloride, bromide, or mixtures thereof, and is most preferably a methosulfate ion. The salt anion may also, however, be nitrate, hydroxide, acetate, or mixtures of these.

15

Illustrative of the numerous patents which describe organic cationic salts, their manner of preparation and their use in the preparation of organophilic clays are commonly assigned U.S. Pat. Nos. 2,966,506, 4,081,496, 4,105,578, 4,116,866, 4,208,218, 4,391,637, 4,410,364, 4,412,018, 4,434,075, 4,434,076, 4,450,095 and 4,517,112, the contents of which are incorporated by reference.

20

The inclusion of the polar aprotic solvent in the organoclay compositions of the present invention gives rise to the particularly advantageous properties of the resultant organoclays of the present invention. When used to activate the organoclays of the present invention, the organoclays exhibit improved dispersion characteristics since the polar aprotic solvent intercalates into the galleries of the organoclay, such as montmorillonite, to aid in the separation of the layer.

25

Modification of the dry processed organoclay, for instance, montmorillonite, with a polar aprotic solvent such as propylene carbonate enables the organoclay to disperse in and thicken solvent-based systems.

- 5 Using the polar aprotic solvent, such as propylene carbonate, to aid separation of clay platelets during processing results in a dry process organoclay with improved characteristics. For instance, dry process organoclays have been prepared that yield 20-150% higher viscosities (depending upon shear rate) in an oil-based paint formulation, than the use of a typical organoclay, Claytone AF, which is an easy-  
10 dispersing, activator-free, wet processed organoclay.

Preferred embodiments of the present invention will utilize a polar aprotic solvent such as propylene carbonate, in combination with a smectite-type clay such as montmorillonite or bentonite, and a quaternary ammonium compound of formula I,  
15 such as dimethyl di(hydrogenated tallow) ammonium chloride (2M2HT), benzyl methyl di(hydrogenated tallow) ammonium chloride (BDT) and dimethyl 2-ethylhexyl hydrogenated tallow ammonium chloride (HTL8).

The amount of the polar aprotic compound and quaternary ammonium compound  
20 reacted with the smectite-type clay depends upon the specific clay, and the specific product in which the clay is to be utilized. Thus, for example, when montmorillonite is used, the amount of polar aprotic solvent, e.g. propylene carbonate, used to activate the clay will range from about 1 to about 60 and preferably from about 10 to about 30, percent by weight. Typically, the amount of  
25 the quaternary ammonium compound ranges from about 0.1 to about 150%, preferably from about 70 to about 130% of the cation exchange capacity of the clay. Thus, for example, when bentonite is used, the amount of cation reacted with the clay will range from about 65 to about 143 milliequivalents, preferably from about 90 to about 124 milliequivalents per 100 grams of clay, 100% active basis.

Optionally, but preferably, the activated organoclay is then dried, and milled to a suitable size, for use as a dry process ingredient in solvent formulations. Typically, the activated organoclay is utilized in the preparation of solvent-based resinous compositions, and especially in compositions such as solvent-based paints. Due to  
5 the unique characteristics of the organoclay, it can be directly added to the paint composition without prior dispersion in solvent. The obvious consequence of such addition is a substantial cost savings due to the use of solvent in the process, and time involved in the additional usual step of pre-dispersion before addition.

- 10 An organoclay composition of the present invention can be prepared by admixing smectite-type clay with a polar aprotic solvent and a quaternary ammonium compound to exchange the counterions that are naturally present in the smectite-type clay. The reaction is typically conducted at ambient temperature or above for a period of time sufficient for the polar aprotic solvent to react with the clay particles.  
15 The method of mixing can involve any type of standard mixer or extruder capable of providing enough shear to initiate the reaction of the clay with the organic materials.

The amount of the polar aprotic solvent added to the smectite-type clay for the  
20 purposes of this invention must be sufficient to impart to the clay the enhanced characteristics desired. The milliequivalent ratio is defined as the number of milliequivalents of the polar aprotic solvent or quaternary ammonium compound, per 100 grams of clay, 100% active basis. The typical smectite-type clays of this invention have a milliequivalent ratio of from about 10 to about 150. The preferred  
25 milliequivalent ratio will vary depending on the characteristics of the particular polar aprotic solvent utilized and the end use for the resultant product.

When the organoclay composition of the present invention is utilized for its rheological properties for application as to control sagging of fluid films and  
30 prevent settling and hard packing of pigments present in paint compositions, it is

typically employed in an amount of about 1 lb. to about 95 lb./100 gallons paint composition.

The present invention thus contemplates the preparation of solvent-based paint formulations having improved properties which comprise the addition of an activated organoclay composition which is the product of a smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay, a polar aprotic compound, and a quaternary ammonium compound. Typically, the paint formulation will contain the improved organoclay composition in an amount of about 0.1 to about 10% by weight of the finished paint formulation. Preferred formulations contain the organoclay thixotrope in an amount of about 3 to about 6% by weight of the finished paint formulation.

The invention will now be illustrated by a series of Examples, which are intended to set forth typical and preferred procedures to be utilized in the practice of the invention. While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

20

### EXAMPLE 1

#### Procedure for the Preparation of Dry Process Organoclays

1. The desired amount of sodium montmorillonite was placed into the steel cup of a Waring-type blender.
- 25 2. The required amount of propylene carbonate (0, 15, 30% per active weight of clay) was added, and the composition was mixed for 10 minutes at a speed appropriate to ensure complete homogeneity.

3. The required amount of quaternary ammonium compound (95 milliequivalents of quat per 100 g clay) was added, and the composition was mixed ten (10) additional minutes at a speed appropriate to ensure complete homogeneity.

- 5 4. The products were dried and milled to the desired particle size.

Quaternary ammonium compounds employed in the study were dimethyl di(hydrogenated tallow) ammonium chloride (2M2HT), benzyl methyl di(hydrogenated tallow) ammonium chloride (BDT), and dimethyl 2-ethylhexyl hydrogenated tallow ammonium chloride (HTL8).

- 10 X-ray d-spacings for the product organoclays are given in Table 1 below.

TABLE 1

Sample #	Quat	% Propylene Carbonate	d-spacing (Angstroms)
1	2M2HT	0	32.557
2	2M2HT	15	31.322
3	2M2HT	30	31.522
4	BDT	0	34.845
5	BDT	15	34.126
6	HTL8	0	31.322
7	HTL8	15	29.286
8	HTL8	30	26.471

The results demonstrate that materials with improved dispersability can be prepared without an increase in clay layer d-spacing, which is remarkable.

EXAMPLE 2Demonstration of Organoclay Improvement

Samples of a typical solvent based paint were prepared using Samples 1-8, prepared in Example 1, above. Brookfield viscosity measurements can be used as a measure of the efficiency of the organoclay, and these results are shown in Table 2 below.

TABLE 2 - Viscosity (cP)

Sample	1 rpm	10 rpm	100 rpm
1	2000	1460	1036
2	6000	2580	1370
3	7000	2820	1428
4	4600	2260	1276
5	6600	2740	1420
6	1400	1240	978
7	4600	2340	1366
8	7000	3020	1522
Control A	2800	1740	1132
Control B	2800	1720	1186
Control C	2200	1580	1128
Control D	600	700	684

Control A = Claytone AF

Control B = Sample 1 with propylene carbonate added to the formulation after the clay

Control C = Claytone 50 with propylene carbonate added to the formulation after the clay

Control D = formulation containing no dry clay.

The results clearly indicate that the addition of the aprotic polar compound, propylene carbonate, results in an improvement in the efficiency of the organoclay.

### EXAMPLE 3

#### Preparation of Dry Process Organoclays

- 5    1.    55 grams of 325 mesh crude Wyoming sodium bentonite is placed into the steel cup of a Waring-type blender.
2.    The required amount of propylene carbonate (0, 15, 30% per active weight of clay) was added, and the composition was mixed for 2 minutes at high speed.
3.    The mixing is stopped, and the clay redistributed in the mixer.
- 10   4.    Steps 2 and 3 are repeated twice, for a total mixing time of 6 minutes.
5.    With the blender stopped, the appropriate amount of the quaternary ammonium salt was added.
6.    The mixture is then mixed for 2 minutes on high setting.
7.    The mixing is stopped and the clay redistributed.
- 15   8.    Steps 6 and 7 are repeated twice so that the total mixing time is 6 minutes.
9.    The resultant product is dried for 2 hours at 110°C in a static oven.
10.   The dried mixture is milled by one pass through the Fritch Pulverisett using a 0.2 mm screen. The dry grind on these clays was not determined.
- 20   In the following tables of Examples 3-4, the composition of the dry process clays will be indicated using a shorthand notation, for example, 20/95 BDT. This indicates that 20% propylene carbonate is added, as based on the weight of the clay, and then the designated quat BDT (benzyl methyl ditallow ammonium chloride) is added in amounts to equal 95 Milliequivalent Ratio (MER). For material made with dimethyl
- 25   di(hydrogenated tallow) ammonium quat, the designation 2M2HT is used.



Initial investigations involved making a propylene carbonate and MER scan using both the BDT and 2M2HT quats. Once the dry process organoclays were produced, they were evaluated by incorporation into the standard paint formula as follows.

**Paint Formula  
TS-034A**

5

**Base:**

To a gallon container add:

Medium Oil Alkyd	1100.0 grams
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CR 800 (TiO <sub>2</sub> )	1430.0 grams
Raybo	27.5 grams
Mineral Spirits	220.0 grams

Disperse 1 hour at 5000 RPMs on Premier Mill

15

Let set overnight, then add:

Base	252.5 grams
Organoclay	3.5 grams

Disperse for 10 minutes at 5000 RPMs

20

Then let down with:

Medium Oil Alkyd	130.0 grams
Mineral Spirits	35.0 grams
Cobalt Dryer	0.7 grams
Zirconium Dryer	1.4 grams
Calcium Dryer	2.5 grams
Anti-Skinning Agent	0.5 grams

25

Shake by hand for 20 seconds and let set overnight. Then shake for 5 to 10 seconds, let set for one hour and then run tests.

The results of these evaluations are given in Tables 3A and 3B. The results of these tests clearly indicate that the dry process organoclay material prepared using a BDT quaternary ammonium is more efficient regarding Brookfield viscosities. Stormer KU viscosities are very similar, as are the dispersion and other characteristics, when

comparing the BDT-based clays to those made with 2M2HT. The exceptions were the dry processed samples made with 20% propylene carbonate and reacted with BDT at either 95 or 85 MER. These samples displayed not only a superior Brookfield viscosity but also a superior Stormer viscosity.

**Table 3A**  
**Dry Process Organoclay - BDT**  
**TS-034A Paint Formula**

Sample ID %PC/BDT MFR (LOI)	Brookfield Viscosity			Stormer KU	Dispersion					Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		3 Min.	5 Min.	10 Min.	15 Min.	24 Hrs.				
20/95 BDT (44.7)	5000	1800	1000	82	5	5	6 ws	6-1/2 ss	6-1/2	7	6	3.0	90.9
20/85 BDT (44.0)	6000	2200	1220	89	5	5	6 ss	6+	6-1/2	7	6	3.6	90.6
20/75 BDT (41.4)	4000	1200	570	71	5 ws	5 ws	5+	6 ss	6 ss	6	6	1.9	90.6
20/65 BDT (39.9)	2000	900	500	70	4+	5 ws	5 ws	5 ss	5 ss	4	8	2.0	89.6
10/95 BDT (44.6)	3000	1100	530	70	6 ws	6 ws	6 ws	6	6-1/2	6	7	1.9	90.3
10/85 BDT (42.6)	4000	1100	570	71	6 ws	6 ss	6 ws	6 ws	6	6	7	2.0	90.3
10/75 BDT (40.1)	3000	1000	516	70	4-1/2	4-1/2	5-1/2	5-1/2	5-1/2	4	6	2.0	87.5
10/65 BDT (37.7)	2000	900	480	70	4	4+	5	5	5	4	8	1.9	90.7

0/95 BDT (47.8)	3000	1100	510	70	5	5	5	5	5	5+	5+	6	8	2.2	91.3
0/85 BDT (39.7)	3000	1000	500	69	5	5	5	5	5	5-1/2	5-1/2	4	7	2.0	91.6
0/75 BDT (36.9)	2000	800	440	67	5+	5+	5+	5+	5+	5+	5+	4	8	1.8	91.2
Control	1000	500	430	67	--	--	--	--	--	--	--	2	10	2.1	90.0

ss = scattered specks

ws = with specks

LOI = loss on ignition

**Table 3B**  
**Dry Process Organoclay - 2M2HT**  
**TS-0034A Paint Formula**

Sample ID %PC/2M2HT (LOI)	Brookfield Viscosity			Stormer KU	Dispersion				Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		3 Min.	5 Min.	10 Min.	15 Min.				
20/95 2M2HT (42.1)	3000	1100	550	70	5ws	5ws	5+ ss	6+ ss	5	7	2.1	90.6
20/85 2M2HT (41.2)	3000	1000	560	70	5-1/2 ws	5+ ws	5 ws	6+ ws	4	8	2.0	90.5
20/75 2M2HT (39.3)	3000	1100	560	72	5ws	5ws	5ss	6ws	5	7	2.0	90.7
20/65 2M2HT (38.0)	2000	800	490	68	5ws	5ws	5ss	6ws	4	9	2.1	90.5
10/95 2M2HT (41.5)	4000	1100	570	71	5ws	5+ ws	6	6	5	8	2.0	90.6
10/85 2M2HT (39.6)	3000	1100	580	71	5ws	5ws	5ss	5ss	4	8	2.1	91.1

10/75 2M2HT (37.4)	2000	900	490	70	4+ ws	4-1/2	5ss	5ss	5ss	4	8	2.0	90.3
10/65 2M2HT (34.9)	1000	700	460	69	3	3+	4ws	4-1/2	4-1/2 ss	4	9	2.2	89.6
0/95 2M2HT (38.9)	2000	9000	480	68	2	3	5+ss	6ws	6ss	3	8	1.9	91.1
0/85 2M2HT (38.3)	2000	800	460	68	3	5ss	6ss	6ss	6ss	3	9	2.3	91.4
0/75 2M2HT (34.5)	2000	800	470	68	4	5ws	5	5+	5+	4	8	1.9	90.9
Control	--	300	280	--	--	--	--	--	7	0	10	1.8	89.4

ss = scattered specks

ws = with specks

LOI = Loss on Ignition

These results indicate that sample paint formulations produced with BDT display superior rheological characteristics (viscosity and sag) as compared to samples prepared with the Claytone AF standard.

EXAMPLE 4

The organoclays prepared in Example 3 were also evaluated by incorporation into the standard paint formula (Soya Oil Formula TS-034S) as follows.

**Paint Formula  
TS-034S**

5

**Base:**

In a gallon container, add:

	Medium Oil Alkyd	1100.0 grams
	CR 800 (TiO <sub>2</sub> )	1430.0 grams
10	Raybo	27.5 grams
	Mineral Spirits	220.0 grams

Disperse 1 hour at 5000 RPMs on Premier Mill

Let set overnight, then add:

	Base	252.5 grams
15	Organoclay	3.5 grams

or as needed

Disperse for 10 minutes at 5000 RPMs

Then let down with:

	Medium Oil Alkyd	130.0 grams
20	Mineral Spirits	17.5 grams
	Soya Oil	17.5 grams

	Cobalt Dryer	0.7 grams
	Zirconium Dryer	1.4 grams
	Calcium Dryer	2.5 grams
25	Anti-Skinning Agent	0.5 grams

Shake by hand for 20 seconds and let set overnight.

Then shake for 5 to 10 seconds, let set for one hour and then run tests.

The results obtained are shown below in Table 4.

Control is paint formulation without any thiotrophic.

**Table 4**  
**Comparisons in Soya Oil Formula**  
**TS-034S**

Sample ID %PC/BDT MER (LOI)	Brookfield Viscosity			Stormer KU	Dispersion					Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		3 Min.	5 Min.	10 Min.	15 Min.	24 Hrs.				
20/95 BDT	4400	1280	630	71	5- 1/2	5 1/2	6ws	6ws	6ws	6	7	2.1	91.9
20/85 BDT	4400	1380	678	74	4	5	5+	6ws	6ws	6	7	2.2	91.6
10/95 BDT	5000	1440	670	73	5	5+	6	6	6	6	7	2.1	91.6
10/85 BDT (42.6)	4000	1100	570	71	6 ws	6 ss	6 ws	6 ws	6 ws	6	7	2.0	90.3
10/75 BDT (40.1)	3000	1000	516	70	4-1/2	4-1/2	5-1/2	5-1/2	5-1/2	4	6	2.0	87.5
10/65 BDT (37.7)	2000	900	480	70	4	4+	5	5	5	4	8	1.9	90.7
0/95 BDT (47.8)	3000	1100	510	70	5	5	5	5+	5+	6	8	2.2	91.3



0/85 BDT (39.7)	3000	1000	500	69	5	5	5	5-1/2	4	7	2.0	91.6
0/75 BDT (36.9)	2000	800	440	67	5+	5+	5+	5+	4	8	1.8	91.2
Control	1000	500	430	67	--	--	--	7	2	10	2.1	90.0

ss = scattered specks

ws = with specks

These results indicate that the rheological performance of optimum Dry Processed Organoclays in Soya containing paints is acceptable, although it was slightly lower than standard production wet process organoclays.

EXAMPLE 5

Evaluation of Selected Press Cake, Dry Process and Competitive Organoclays in a Post Add Formula (Formula TS-033):

The same clays used in Example 4 were then evaluated for their ease of dispersion  
5 using our TS-033 Formula as follows:

**Formula 1****TS-033****White Architectural Enamel**

1. To the mixer bowl of a Poly Mill, add:  
10 Medium Oil Alkyd 500.0 grams  
Raybo HS-57 17.0 grams  
Mineral Spirits 90.0 grams

Lower impeller and start mill at low speed  
(500 RPM).

- 15 TiO<sub>2</sub> 1129.0 grams

Increase mill speed to 1000 RPMs and mill for 45  
minutes.

2. Reduce mill speed to 500 RPMs and add:  
20 Medium Oil Alkyd 500.0 grams

Mix at 500 RPMs for 10 minutes.

3. Stop mill and discharge grind paste into 1 gallon can.

4. Add to the Poly Mill bowl:  
25 Mineral Spirit 356.0 grams

Run mill for 2 minutes and discharge the mineral spirits into the  
gallon can containing the grind paste.

5. To the gallon can containing the grind paste, add:
 

Medium Oil Alkyd	1101.0 grams
Calcium Dryer	12.0 grams
Zirconium Dryer	23.0 grams
Anti-Skinning Agent	8.0 grams
- 5 Place under dispermat equipped with 80 mm blade and mix at 1000 RPMs for 10 minutes.
6. Seal gallon lid and place on a paint shaker and shake for 5 minutes.
- 10 7. After shaking, divide the paint into pint cans, each containing 280 grams of paint.
- 15 8. Place pint can containing 280.0 grams of paint under a dispermat equipped with a 40 mm blade and start mixing at 1000 RPM's. Weigh out 3.0 grams of organoclay to be tested and slowly add the organoclay to the pint can. When all the organoclay has been incorporated, increase the blade speed to 1300 RPMs. Disperse for 25 minutes.
9. After dispersing, seal the pint can with a lid and place in the controlled temperature bath and allow to stand overnight.
- 20 10. After standing overnight, measure desired parameters.

Table 5 presents the data obtained from testing. The results indicate that Brookfield viscosities for most samples were similar. The exception was Claytone AF which had lower Brookfield viscosities. Dispersion for the Dry Process material reached 6-1/2.

**Table 5**  
**Comparisons in Post Add Formula**  
**TS-033**

Sample ID	Brookfield Viscosity			Stormer KU	Dispersion				Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		5 Min.	10 Min.	15 Min.	25 Min.				
20/95 BDT	4000	1380	718	76	0	6-1/2 w	6-1/2 w	6-1/2 s	7	7	2.3	91.8
20/85 BDT	4000	1400	710	78	0	6-1/2 w	6-1/2 w	6-1/2 s	7	7	2.4	90.4
10/95 BDT	3400	1250	678	75	0	6w	6w	6+w	6	8	2.4	86.3
CT AF	2400	1040	614	74	0	2	7w	7	6	8	2.3	90.3
BT SD-1	3200	1180	659	75	4	6w	7s	7	6	8	2.4	91.2
MP-100	4000	1380	720	79	0	0	6w	7w	7	7	2.6	89.5
Control	500	400	382	68	--	--	--	--	3	10	2.2	87.3

w = with specks; s = some specks

The 20 minute grind results and the 20° and 85° were taken but are not reported. They can be found in HRD's lab notebook #47 Page 119 dated 6-17-96.

CT AF designates Claytone AF

BT SD-1 designates Bentone

MP-100 designates Thiogel MP-100

EXAMPLE 6

Other process were evaluated to determine what effect, if any, the process had upon the properties of the desired endproduct. Propylene carbonate levels and shear used while incorporating the propylene carbonate were investigated as possible variables.

- 5 Other variables checked were the drying and fineness of milling. The samples listed as course milled plugged the Fritch Pulverisett mill, so no further milling was done.

Dry Process samples were prepared using 325 mesh sodium bentonite in a process similar to that described in Example 3. The samples are described as follows in Table 6A below:

TABLE 6A

Sample ID	%PC	P.C. Incorporation Shear	Drying	Milling	% Moist.	LOI
106A	4	3 times, each one for 2 min.	No	Coarse	2.4	40.9
106A Dry	4	3 times, each one for 2 min.	Yes	Fine	1.1	40.9
107A Dry	4	3 times, each one for 5 min.	No	Coarse	2.0	41.5
107A Dry	4	3 times, each one for 5 min.	Yes	Fine	1.1	41.1
107B	10	3 times, each one for 2 min.	No	Coarse	2.7	42.9
107B Dry	10	3 times, each one for 2 min.	Yes	Fine	1.7	42.3
108A	10	3 times, each one for 5 min.	No	Coarse	2.5	42.4
108A Dry	10	3 times, each one for 5 min.	Yes	Fine	1.8	41.7

%PC = Percent propylene carbonate as based on the clay.

LOI (loss on ignition) results on the above samples indicate the presence of more organic, i.e., propylene carbonate in the high treatment propylene carbonate; however, not as much as would be expected. Based on the theoretical, about 1% propylene carbonate was lost in the samples in which 4% was added; whereas 6% propylene carbonate was lost in the samples in which 10% was added. This loss is suspected to be due to volatilization during incorporation in the Bentonite clay.

These samples were evaluated, as were other samples, in the above-described TS-033 formula for dispersibility. Table 6B below presents the results.



**Table 6B**  
**Propylene Carbonate**  
**Incorporation Variables**  
**TS-033 Formula**

Sample ID	Brookfield Viscosity			Stormer KU	Dispersion					Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		5 Min.	10 Min.	15 Min.	25 Min.	24 Hrs.				
20/95 BDT	4800	1440	684	76	0	6w	6+s	6+	6+	6	7	2.2	92.4
10/95 BDT	5400	1520	678	74	0	6w	6s	6+	6+	7	6	2.2	92.3
106A (L,L)	4000	1280	628	76	0	0	0	0	4	6	7	2.2	88.0
106A Dry (L,L)	3000	1160	598	73	0	2	2	4w	--	5	7	2.2	85.8
107A (L,H)	3600	1220	606	74	0	0	0	0	4w	5	7	2.2	90.4
107A Dry (L,H)	3600	1220	606	73	0	2	4w	5w	5w	5	7	2.2	90.2

107B (H,L)	5200	1620	742	77	0	0	0	6w	6w	6w	7	6	2.2	90.9
107B Dry (H,L)	5000	1500	698	77	0	6w	6w	6+	6+	6+	7	6	2.2	91.8
108A (H,H)	5400	1580	728	78	0	0	0	6w	6w	6w	7	6	2.2	91.1
108 Dry (H,L)	4200	1520	714	78	0	3-1/2	5w	6s	6+s	6+s	7	6	2.2	91.0
CTAF	3600	1200	608	75	2	6w	7w	7s	7	7	5	7	2.2	91.2
Control	800	460	422	67	--	--	--	--	7	7	3	10	2.1	90.0

W = With Specks; S = Some specks.

CT AF designates Claytone AF, a commercially available organoclay.

Designations in parenthesis, first letter

L = level of propylene carbonate of 4%

H = level of propylene carbonate of 10%

second letter

L = shear time of 2 minutes

H = shear time of 5 minutes

- General conclusions can be drawn from the data presented in Table 6B. Samples containing the 10% propylene carbonate addition had higher Brookfield viscosities as compared to the samples containing 4%. Also, samples that were dried and fine milled displayed faster dispersion with the sample containing 10% propylene carbonate displaying more complete dispersion. The samples which were coarse milled displayed higher Brookfield viscosities as compared to the fine milled samples; however, the grind characteristics for these coarse milled samples were poor. Samples with 10% propylene carbonate compared well to previously produced Dry Processed material and better than Claytone AF.
- 10 Based on this information, the optimum level of propylene carbonate based on the clay weight appears to be about 10% for a Dry Process organoclay.

#### EXAMPLE 7

- Variation in the Process of Preparation of the Dry Processed Organoclay:  
Three Dry Process organoclay samples were made by varying the  
15 production/incorporation process in order to determine optimum parameters. These organoclays were made as described below.

Pilot plant produced Dry Process organoclay was made according to the following procedure:

- Bentonite + quaternary ammonium salt at a level of 85mer → dry → coarse mill to 200  
20 mesh → addition of Propylene Carbonate (10% based on weight of bentonite) → mill to 90% < 450 mesh.

- A shortened version of this process was conducted according to the following procedure: Bentonite and the particular quaternary ammonium salt at a level of 85 mer → shear → addition of Propylene carbonate (10% based on weight of bentonite) →  
25 dry → mill to 90% < 450 mesh.

A third version was prepared using a Drais Rapidmixer T-160. The procedure was as follows: Bentonite and the particular quaternary ammonium salt at a level of 95 mcr → dry → mill → addition of propylene carbonate (5% based on weight of bentonite → mill to 90 < 450 mesh.

- 5 The final moisture and LOI on the above samples are listed in the following Table 7A.

**Table 7A**

Sample	Moisture	% LOI
Pilot Plant	3.0	41.7
Shorten Process	3.5	42.0
Drais Rapidmixer	3.5	38.3

These samples were then evaluated and compared to commercially produced organoclays using the above-described standard paint Formula 1 (TS-033 Formula). Results are presented in Table 7B below.

**Table 7B**  
**Process Variation Evaluations**  
**TS-033**

Sample ID	Brookfield Viscosity			Stormer KU	Dispersion				Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		5 Min.	10 Min.	15 Min.	25 Min.				
Pilot Plant	4700	1690	918	74	0	2	5+s	5+s	7	7	2.1	--
Shorten Process	4700	1630	884	75	0	2	6+s	6-1/2s	7	7	2.1	--
Drais Process	2900	1230	777	70	0	1	3+	5w	6	7	2.0	--
Claytone AF	3100	1280	755	74	2	6w	7w	7	7	8	2.1	--
Control	1100	1000	700	--	--	--	--	--	--	--	1.9	--

W = with specks; S = some specks.

These samples were also evaluated using the above-described standard paint Formula 3 (TS-034A Formula). Results are presented in Table 7C below.

**Table 7C**  
**Process Variation Evaluations**  
**TS-034A**

Sample ID	Brookfield Viscosity			Stormer KU	Dispersion				Sag	Level	ICI Visc.	60° Gloss
	1 RPM	10 RPM	100 RPM		5 Min.	10 Min.	15 Min.	25 Min.	24 Hrs.			
Pilot Plant	4700	1300	582	72	0	6w	6+	--	6-1/2	7	2.1	--
Shorten Process	4200	1210	563	72	0	6w	6+	--	6-1/2s	7	2.2	--
Drais Process	3700	1080	528	70	0	6w	6+	--	6-1/2s	8	2.1	--
Claytone AF	4800	1350	594	73	5	7w	7s	--	7s	7	2.2	--

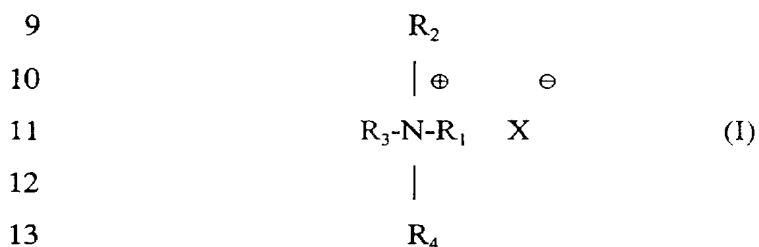
W = With Specks; S = Some Specks.

These results indicate that the shortened process produces a product having very similar Brookfield viscosities as compared to the more lengthy process.



WHAT IS CLAIMED IS:

1. An improved process for the preparation of a solvent-based coating composition which comprises the direct addition thereto, is without prior dispersion in the solvent, of a dry process activated organoclay composition comprising a smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay (active basis), about 1 to about 68 percent by weight (based on the weight of the organoclay) of a polar aprotic solvent selected from the group consisting of propylene carbonate, ethylene carbonate, N,N-dimethylformamide, N,N-dimethylacetamide and dimethyl sulfoxide, and a quaternary ammonium compound of the formula I

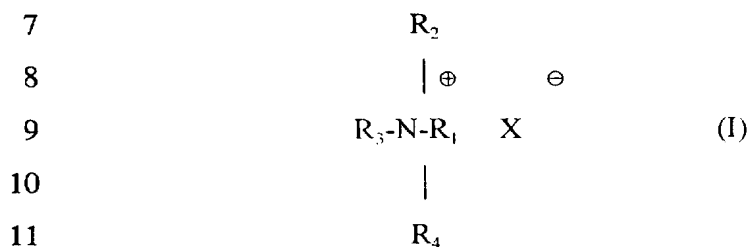


wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are independently selected from the group consisting of linear or branched, saturated or unsaturated alkyl groups having 1 to 22 carbon atoms, aralkyl groups which are benzyl and substituted benzyl moieties, aryl group, beta, gamma-unsaturated groups having six or less carbon atoms, hydroxyalkyl groups having two to six carbon atoms, and hydrogen, with the proviso that at least one of the substituents is a linear or branched saturated or unsaturated alkyl group; and X is the salt anion.

2. The method according to Claim 1 wherein the polar aprotic solvent is present in an amount of about 1 to about 40 percent by weight of the organoclay.

3. The method according to Claim 2 wherein the polar aprotic solvent is present in an amount of about 10 to about 20 percent by weight of the organoclay.

- 1 4. The method according to Claim 3 wherein the polar aprotic solvent is  
2 propylene carbonate.
- 1 5. The method according to Claim 4 wherein the quaternary ammonium  
2 compound of formula I is dimethyl di(hydrogenated tallow) ammonium chloride.
- 1 6. The method according to Claim 4 wherein the quaternary ammonium  
2 compound of formula I is benzyl methyl di(hydrogenated tallow) ammonium chloride.
- 1 7. The method according to Claim 4 wherein the quaternary ammonium  
2 compound of formula I is dimethyl 2-ethylhexyl hydrogenated tallow ammonium  
3 chloride.
- 1 8. The method according to Claim 1 wherein the smectite-type clay is  
2 montmorillonite.
- 1 9. The method according to Claim 1 wherein the smectite-type clay is bentonite.
- 1 10. An improved rheological additive composition which comprises an activated  
2 organoclay composition comprising a smectite-type clay having an ion exchange  
3 capacity of at least 50 meq. wt. per 100 g. clay (active basis), a polar aprotic  
4 compound such as propylene carbonate, ethylene carbonate, N,N-dimethylformamide,  
5 N,N-dimethylacetamide and dimethyl sulfoxide and others, and a quaternary  
6 ammonium compound of the formula I



12 wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from the group consisting of  
13 linear or branched, saturated or unsaturated alkyl groups having 1 to 22 carbon atoms.  
14 aralkyl groups which are benzyl and substituted benzyl moieties, aryl group, beta,  
15 gamma-unsaturated groups having six or less carbon atoms, hydroxyalkyl groups  
16 having two to six carbon atoms, and hydrogen, with the proviso that at least one of the  
17 substituents is a linear or branched saturated or unsaturated alkyl group; and X is the  
18 salt anion.

1 11. The method according to Claim 10 wherein the polar aprotic solvent is present  
2 in an amount of about 1 to about 40 percent by weight of the organoclay.

1 12. The method according to Claim 11 wherein the polar aprotic solvent is present  
2 in an amount of about 10 to about 20 percent by weight of the organoclay.

1 13. The method according to Claim 12 wherein the polar aprotic solvent is  
2 propylene carbonate.

1 14. The method according to Claim 13 wherein the quaternary ammonium  
2 compound of formula I is dimethyl di(hydrogenated tallow) ammonium chloride.

1 15. The method according to Claim 13 wherein the quaternary ammonium  
2 compound of formula I is benzyl methyl di(hydrogenated tallow) ammonium chloride.

1 16. The method according to Claim 13 wherein the quaternary ammonium  
2 compound of formula I is dimethyl 2-ethylhexyl hydrogenated tallow ammonium  
3 chloride or methosulfate.

1 17. The method according to Claim 10 wherein the smectite-type clay is  
2 montmorillonite.

1 18. The method according to Claim 10 wherein the smectite-type clay is bentonite.

1 19. A solvent-based paint composition which comprises an activated organoclay  
2 according to Claim 10 in an amount of about 1 lb. to about 95 lb./100 gallons paint  
3 composition.

1 20. A solvent-based paint composition which comprises an activated organoclay  
2 according to Claim 14 in an amount of about 1 lb. to about 95 lb./100 gallons paint  
3 composition.

1 21. A solvent-based paint composition which comprises an activated organoclay  
2 according to Claim 15 in an amount of about 1 lb. to about 95 lb./100 gallons paint  
3 composition.

# INTERNATIONAL SEARCH REPORT

In. .national application No.  
PCT/US97/03013

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : CO4B 14/00, 14/10, 33/02; C09C 1/42

US CL : 106/486, 487; 501/148; 252/315.2

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/486, 487; 501/148; 252/315.2

IPC(6): C04B 14/00, 14/10, 33/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
none

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,425,244 A (HOUSE) 10 JANUARY 1984, SEE COLUMN 5, LINE 46-COLUMN 9, LINE 60.	1-21
Y	US 4,382,868 A (HOUSE) 10 MAY 1983, SEE COLUMN 2, LINE 52-COLUMN 6, LINE 64.	1-21
Y	US 5,186,747 A (MATTINGLY) 16 FEBRUARY 1993, SEE COLUMN 2, LINE 16-COLUMN 5, LINE 17.	1-21
Y	US 5,358,562 A (NAE ET AL.) 25 OCTOBER 1994, SEE COLUMN 2, LINE 53-COLUMN 5, LINE 16.	1-21
Y	US 4,743,305 A (DOIDGE ET AL.) 10 MAY 1988, SEE COLUMN 1, LINE 2-COLUMN 2, LINE 36.	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 08 APRIL 1997	Date of mailing of the international search report 11 JUL 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Michael Marcheschi</i> MICHAEL MARCHESCHI Telephone No. (703) 308-0661